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Synthesis of Carboranes from Dihydrocarboranes

by

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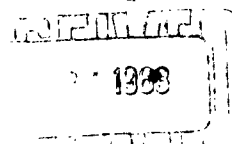
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Synthesis of Carboranes from Dihydrocarboranes¹

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ABSTRACT

Carborane-2,5 is the major volatile carborane formed from the pyrolysis of dihydrocarboranes-2,4. The presence of trimethylamine during the pyrolysis significantly increases the yield of sym-carborane-2,4.

The carboranes sym-C₂B₃H₅, unsym-C₂B₄H₆, sym-C₂B₄H₆ and C₂B₅H₇ have been prepared in a silent electric discharge in very low yields^{3,4}. Since a high

3. R. E. Williams, D. D. Good and I. Shapiro Abstracts, 140th Amer. Chem. Soc. Meeting, Chicago, Illinois. September (1961) p. 14 N; J. Amer. Chem. Soc., 84, 3837 (1962).
 4. C. D. Good and R. E. Williams, U.S. Patent No. 3,030,289 (1962).
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yield synthesis of the C-alkylderivatives⁵ of C₂B₄H₈⁶ has been discovered, it was

5. T. P. Onak, R. E. Williams and H. G. Weiss, J. Amer. Chem. Soc., 84, 2830 (1962).

6. The discovery of the parent dihydrocarborane, $C_2B_4H_8$, by H. G. Weiss and its isolation by C. D. Good³ has been reported; I. Shapiro, Pacific Coast Conf. Anal. Chem. and App. Spectroscopy, Pasadena, Calif., Dec. (1962).
-

decided that catalytic removal of H_2 or removal of BH_3 by a Lewis base might lead to the preparation of C-alkylderivatives of $C_2B_4H_6$ and $C_2B_3H_5$,⁷ respectively.

7. We subscribe to the suggestion⁸ that $C_2B_3H_5$ is better than $B_3C_2H_5$ in that it reflects the carbon boron order in the name; it would appear that carborane-2,3 would be better than carborane-3 or triboradimethyne since carboranes with 4 or 6 etc. carbons and hydrocarboranes with more or less than two carbons will probably be discovered.
8. R. Hoffmann and W. N. Lipscomb, Inorg. Chem., 2, 231 (1963).
-

Since loss of H_2 and BH_3 are considered to occur in the related boron hydrides merely by heating, a preliminary experiment was undertaken to determine which reaction was preferred. No alkyl derivatives of $C_2B_3H_5$ were detected from the dihydrocarboranes (perhaps the alkyl groups interfered with the ejection of a BH_3 group). Alkyl derivatives of symmetrical- $C_2B_4H_6$ were isolated; however, no alkyl derivatives of unsymmetrical- $C_2B_4H_6$ ⁹ were observed. Surprisingly,

9. The suggestion that unsym- $C_2B_4H_6$ may rearrange to sym- $C_2B_4H_6$ ⁸ was made when the carboranes were first isolated by Good.^{3,4} This possibility, at elevated temperature, is now under investigation.
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C-alkyl derivatives of $C_2B_5H_7$ were produced in unanticipated abundance.

EXPERIMENTAL

Preparation of dihydrocarboranes. (a) C,C'-dimethyldihydrocarborane-2,4 (Ia)

To 10 ml of 2,6-lutidine (Matheson, Coleman and Bell)¹⁰ were added 17 mmoles of

10. Purified according to the procedure described by H. C. Brown, S. Johnson and H. Podall, J. Am. Chem. Soc., 76, 5556 (1954).

pentaborane (Olin Mathieson) and 30 mmoles of 2-butyne (Columbia). After stirring the mixture for 5 hrs at room temperature the volatile components were vacuum fractionated through traps at -80° and -190° . To the contents in the -80° trap was added 25 ml of freshly distilled boron trifluoride ethyl etherate (Eastman). After stirring the resulting heterogeneous solution for 15 min. at room temperature the volatiles were fractionated through -20° , -80° , and -190° traps. The crude Ia in the -50° trap was stored over 1 gm lithium aluminum hydride for 1 hr and then fractionated through traps at -70° and -190° . The -70° trap contained 0.69 mmoles (40%) of Ia.

(b) C-propyldihydrocarborane-2,4 (Ib). The reaction was carried out in a manner essentially identical to that described above using 30 mmoles of 1-pentyne (Columbia) instead of 2-butyne. The yield of Purified Ib was 0.65 mmoles (38%).

Pyrolysis of dihydrocarboranes to carboranes; (a). - One mmole of dihydrocarborane-2,4 was sealed into a 25 ml flask equipped with a 5 mm (dia.) tube for taking n.m.r. spectra. The lowest temperature at which the disappearance of dihydrocarborane occurred at a reasonable rate is given in table 1. This was determined by following the H^1 n.m.r. while increasing the temperature. After the minimum conditions were applied to decompose 95-100% of the dihydrocarborane, the contents of the flask were gas chromatographed (Table 2). In addition to the volatile carboranes an appreciable quantity of unidentified tan solids formed during the pyrolysis.

Anal. Calcd. for $C_5B_5H_{13}$ (IIb): C, 47.2; B, 42.5; H, 10.3. Found: C, 46.6; B, 42.8; H, 10.5.

(b) Addition of trimethylamine. - The reaction was carried out in a manner essentially identical to that described above; however, 1 mmole trimethylamine (Matheson) was added to the contents of the flask. Tables 1 and 2 summarize the reaction conditions, yield of carboranes and gas chromatographic results. Prior to the gas chromatography of the products the trimethylamine was removed by fractionating through traps at -90° and -190° . Examination of the -190° bath indicated a nearly quantitative recovery of the trimethylamine originally present.

(c) Addition of isobutane. - Using isobutane (Matheson) instead of trimethylamine the pyrolysis was carried out in a manner essentially identical to that described above. After the pyrolysis the reaction mixture was introduced immediately onto the gas chromatographic column for separation.

Gas chromatography was used for final purification of the dihydrocarboranes and carboranes. A 30% Kel-F column on firebrick¹¹ operated at 90° was used. The

11. T. Onak and F. Gerhart, Inorg. Chem., 1 742 (1962).

retention volumes (relative to pentaborane) are given in Table 2.

Mass Spectra were taken on a CEC 21-620 instrument. Table 2 lists the observed parent peaks.

Nuclear Magnetic Resonance Data: B¹¹ n.m.r. spectra were measured with a Varian V-4300 high resolution spectrometer operating at 12.83 Mc (Table 3). H¹ n.m.r. spectra were measured with a Varian A-60 spectrometer (Table 4).

DISCUSSION

C,C'-dimethylcarborane-2,5 (IIa) is the principle volatile carborane formed from the pyrolysis of C,C'-dimethyldihydrocarborane-2,4 (Ia). In addition, a small quantity of C,C'-dimethyl-sym-carborane-2,4 (IIIa) is formed. Similarly, C-n-propyldihydrocarborane-2,4 (Ib) upon pyrolysis yields C-n-propylcarborane-2,5 (IIb) and C-n-propyl-sym-carborane-2,4 (IIIb). Neither of the dihydrocarboranes subjected to pyrolytic conditions gives identifiable amounts of the alkyl substituted carboranes-2,3 or unsym-carboranes-2,4.

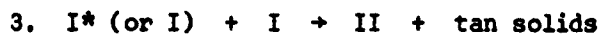
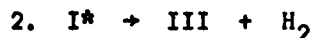
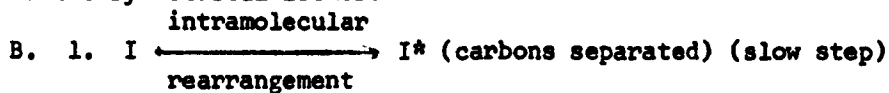
A reaction between trimethylamine (TMA) and dihydrocarborane-2,4 was expected to yield the carborane-2,3 by abstraction of a borane unit; however, no reaction is observed below 250°, and above this temperature the sym-carborane-2,4 and carborane-2,5 are the major volatile carborane products. Within experimental error the TMA is quantitatively recovered. Although the total amount of volatile carboranes remains approximately unchanged when the pyrolysis is carried out in the presence of TMA the relative quantity of the sym-carborane-2,4 is greatly enhanced. Although the TMA could be acting as a diluent during the pyrolysis it is not likely that this is the major cause of the change in product distribution; for when the pyrolysis is carried out in the presence of isobutane, the same product distribution is obtained as when no diluent is used. Apparently, the unshared electrons of TMA play an important part in determining the course of the pyrolysis.¹²

12. Although a detailed discussion of possible mechanisms is preliminary, several working hypotheses appear quite plausible:

- A. 1. $I + \text{unsym-C}_2\text{B}_4\text{H}_6 + \text{H}_2$ (slow step)
2. $\text{unsym-C}_2\text{B}_4\text{H}_6 + \text{III}$
3. $\text{unsym-C}_2\text{B}_4\text{H}_6$ (or I) + I → II + tan solids

If it is assumed that unsym- $C_2B_4H_6$, once formed, does not rearrange at 300°

to the symmetrical isomer:



The presence of trimethylamine might catalyze reactions 1 and 2 (in both A and B schemes) and yet not appreciable affect reaction 3 because catalysis, in this case, would involve a three-body collision.

Before this investigation was undertaken there were several uncertainties with respect to the structure or structures of the $C_2B_5H_7$ compound(s); for the previous B^{11} n.m.r. spectra did not unambiguously demonstrate that only one isomer was present.³ Since the B^{11} n.m.r. spectra (Table 3) of $C_2B_5H_7$, C-n-propyl $C_2B_5H_6$ and C,C'-dimethyl $C_2B_5H_5$ all have quite similar spectra (two different synthetic routes are also involved) it seems probable that a single isomer is produced.

The evidence that $C_2B_3H_5$, and sym- $C_2B_4H_6$'s structurally resemble a trigonal bipyramid and an octahedron, respectively, appear convincing.³ The most likely candidate for the $R_2C_2B_5H_5$ is a pentagonal bipyramid and the B^{11} n.m.r. immediately eliminates a symmetrical structure with carbon at the apexes

of a five boron mutual base. Three other structures (about a pentagonal

bipyramid) are possible wherein three different boron environments are created in the ratio 2:2:1; in two of these structures the carbons are adjacent. Previously, the most likely candidate was one with adjacent carbons for there was no evidence that the carbons from the original acetylene had become separated. During the present investigation it became evident that the $R_2C_2B_4H_4$'s (III, figure 1) produced had non-adjacent carbons which made the structure of $R_2C_2B_5H_5$ (II, figure 1) in which the carbons are nonadjacent more attractive. Two other considerations also recommend this structure: First, the B^{11} n.m.r. resonance assigned to the unique boron (e figure 1) is quite narrow compared to the resonances assigned to the other boron nuclei; the partial isolation of the lone boron (carbons on sides) might account for this. Secondly it seems reasonable that separation of the carbons should lead to a more thermodynamically stable molecular species;¹⁴ certainly sym- $C_2B_4H_6$ is prepared in greater abundance from

14. This has been independantly presumed by W.N. Lipscomb Proc. Natl. Acad. Sci. U.S. 47, 1791 (1961); R. Hoffmann and W.N. Lipscomb, J. Chem. Phys., 36, 3489 (1962).

the pyrolysis than unsym- $C_2B_4H_6$ where the carbons are adjacent. The chemical shifts and spin-spin coupling constants (Tables 3 and 4) are related to the possible structure II (figure 1) for convenience.

The alkane side products produced during the pyrolysis are consistent with the assumption that the skeletal carbon-carbon bond is rather easily broken. Thus, n-butane is formed from the pyrolysis of Ib; however, no pentane is found. It is interesting to note that a considerable amount of propane is formed in addition to n-butane, and yet none of the parent (non-alkylated) carboranes are formed in the process. This may imply that dihydrocarborane and/or carborane

radicals lead to the observed solids.

The observed melting points (Table 2) are in good relative agreement with the symmetry of the proposed structures for the dihydrocarboranes-2,4,⁵ sym-carborane-2,4 and carborane-2,5. The series Ia, IIa, IIIa and the series Ib, IIb, and IIIb represent a progression to greater symmetry; and, therefore one would expect the observed increase in melting point. The "a" compounds, containing methyl substituents on each of the two skeletal carbons melt, expectedly, higher than the "b" compounds with a propyl group on only one of the skeletal carbons.

Although the carborane distribution from the pyrolysis of dihydrocarboranes is not the same that found from the silent electric discharge reaction between pentaborane and acetylene,^{3,4} it is tempting to conclude that the silent discharge production of carboranes proceeds through a dihydrocarborane intermediate. A consequence of this conclusion is the prediction that a silent electric discharge through pure dihydrocarboranes may be a potential synthetic route to $C_2B_3H_5$ and unsym- $C_2B_4H_6$ derivatives.

Table 1

Data for the Conversion of Dihydrocarboranes to Carboranes

Dihydrocarborane	Other material present	Minimum Pyrolytic conditions		Volatile products		
		temp.	hrs.	Carborane-2,5	sym-carborane-2,4	Other
Ia	none	290°	20	IIa, 25%	IIIa, 5%	Ca. 10% alkanes, MS indicating 95% ethane, traces of boron hydrides and possibly traces of propane and butane.
Ib	none	300°	20	IIb, 30	IIIb, 2	ca. 10% alkanes, MS indicating 80% propane, 15% n-butane, traces of boron hydrides and possibly traces of ethane.
Ia	trimethyl-amine	260°	20	IIa, 15	IIIa, 25	Trimethylamine quantitatively recovered.
Ib	trimethyl-amine	280°	6	IIb, 15	IIIb, 20	Trimethylamine quantitatively recovered; however, contaminated with traces of a boron hydride (I.R.).
Ia	isobutane	280°	35	IIa, 30	IIIa, 5	isobutane quantitatively recovered.

Table 2

Physical Data for the Carboranes and Dihydrocarboranes

Compound	Gas chroma- tography; R _v	Mass Spectrum; observed parent peak	Melting point
Ia	2.2	104	-64 to -63
Ib ^a	6.2	not taken	glass
IIa	1.9	114	-30 to -28
IIb ^a	5.4	128	-99 to -97
IIIa	1.1	102	-2 to -1
IIIb	2.4	116	-88 to -87

• ^a Racemates

Table 3

B¹¹ n.m.r. chemical shifts and coupling constants.^a

	<u>e (δ^b, Jc/s)</u>	<u>f or g</u>	<u>g or f</u>
IIa	-5.6, 177	-4.5(est), 165(est)	+19.5, 176
IIb	-5.2, 176	-4.0(est), 170(est)	+21.0, 176
C ₂ B ₅ H ₇ ³	-5.0, 187	-2.0(est), 170(est)	+23.5, 178
<hr/>			
	<u>h</u>		
IIIa	+16.3, 185		
IIIb	+18.6, 186		
sym-C ₂ B ₄ H ₆ ³	+19.4, 189		

a. B¹¹ chemical shifts and coupling constants of the dihydrocarboranes have been reported previously.⁵

b. δ , ppm relative to boron trifluoride ethyl etherate.

Table 4

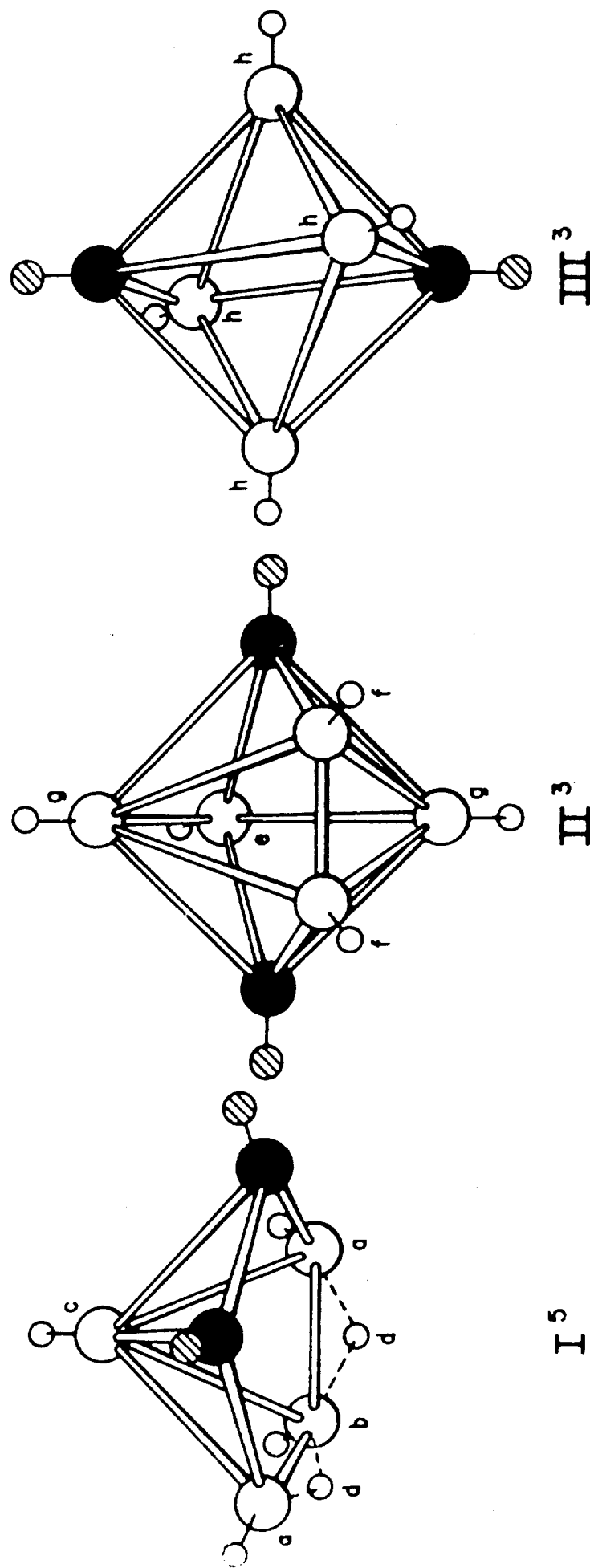
 ^1H n.m.r. Chemical Shifts and coupling constants.

<u>a and b (δ^a, Jc/s)</u>		<u>c</u>	<u>d</u>	<u>i</u>	<u>j</u>	<u>k</u>	<u>l</u>	<u>m</u>
Ia	-3.20, 156	+0.92, 178	+2.4 (est)	-2.07				
Ib	-3.37, 157	+0.85, 180	+2.4 (est)		-0.96	-1.65	-2.40	-6.10
	<u>e</u>	<u>f or g</u>	<u>g or f</u>					
IIa	-4.46, 176	-3.67, 165	-0.18, 175	-2.02				
IIb	-5.2, 180	-4.1 (est) ^b	-0.2, 179		-0.87	-1.57	-2.43	-5.35
C ₂ B ₅ H ₇	-5.0 ^c , 183	-4.3 ^c , 170	-0.2 ^c , 178					-5.7 ^c
	<u>h</u>							
IIIa	-1.83, 184			-1.33				
IIIb	-1.93, 187				-0.94	-1.42	-1.77	-2.87
sym-C ₂ B ₄ H ₆ ³	-1.29 ^c , 190							-2.37 ^c

a. δ , ppm relative to tetramethylsilane, Negative values are to low field.

b. Only the lower member of the quartet was clearly distinguishable. δ was calculated assuming $J = \text{ca. } 170\text{c/s}$ from B11 n.m.r. data (Table 3).

c. Not corrected for bulk susceptibility.



Ball and stick models of dihydrocarborane-2,4, carborane-2,5 and sym-carborane-2,4. No attempt is made to depict these structures in terms of two and three center bonds since we wish to avoid the problems associated with the valence bond structural ellipsis⁵ implied even by a sophisticated representation⁸. For further discussion on this subject see Lipscomb and coworkers, J. Chem. Phys., 35 1329 (1961); and ref. 14.

Fig. 1. \bigcirc Boron; \bigcirc Hydrogen; \bullet Carbon; \textcircled{h} R and R'

(a) $\frac{R}{i}$ CH_3^- $\frac{R'}{i}$ CH_3^-

(b) $\frac{j}{k} \frac{l}{m}$ $\text{CH}_3\text{CH}_2\text{CH}_2^-$ H^-

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